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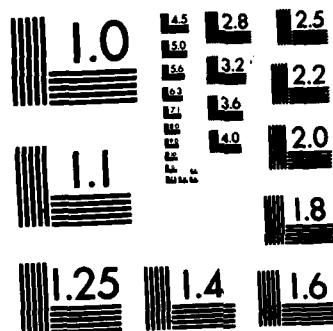
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Inelastic Electron Tunneling Spectroscopic Study of Acetylene
Chemisorbed on Alumina Supported Palladium Particles

by

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Inelastic electron tunneling spectroscopic study of acetylene
chemisorbed on alumina supported palladium particles

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ABSTRACT

Inelastic electron tunneling spectroscopy was used to study the adsorption of acetylene on palladium particles supported by alumina. Low peak intensities in the spectra complicated the analysis of the multiple species present. Nevertheless, some species could be tentatively identified including weakly bonded acetylene, two types of strongly bonded acetylenic species and two other further rehybridized species. The prospect for the future application of tunneling spectroscopy to the study of other hydrocarbons adsorbed on model supported metal catalysts is discussed.

INTRODUCTION

Recently, inelastic electron tunneling spectroscopy has been applied to the study of chemisorption and catalysis. On model supported metal catalysts, the chemisorption and hydrogenation of carbon monoxide on rhodium,¹⁻³ iron,⁴ nickel⁵ and cobalt⁶ and the chemisorption of ethanol on silver clusters⁷ have been examined. Adsorption of unsaturated nitrile,⁸ cobalt and nickel glycinate⁹ and zirconium tetraborohydride¹⁰ have been studied. Adsorption of unsaturated hydrocarbons on aluminum oxide and magnesium oxide have also been investigated using tunneling spectroscopy.^{11,12}

The adsorption and hydrogenation of unsaturated hydrocarbons on group VIII transition metal catalysts are of both practical and fundamental importance. Thus, they have been studied by a variety of techniques. In particular, the adsorption of acetylene (C_2H_2) on palladium has been examined by infrared spectroscopy,¹³⁻¹⁸ high resolution electron energy loss spectroscopy,¹⁹ ultraviolet photoelectron spectroscopy^{20,21} and gas adsorption measurements.^{22,23}

As a natural extension of our previous work, we investigated the applicability of tunneling spectroscopy to the study of adsorption of hydrocarbons on model supported metal catalysts. Here, we present a study of acetylene (and deuterated acetylene) chemisorption and decomposition on alumina supported palladium. Tunneling spectra of these samples show a wide variety of species. Our attempts to isolate these species, even with isotopic studies to guide us, were not successful. This and very low peak intensities complicated the assignment of the spectra.

Currently, the accepted method for analyzing vibrational spectroscopic data of surface species is by comparison with relevant model compounds of known molecular structure. We have taken this approach in our analysis of acetylene adsorbed on alumina supported palladium particles. By comparison with suitable model compounds, we can tentatively identify weakly adsorbed acetylene, two types of tightly bonded acetylene and characterize two other species by their state of hybridization. We also observed the decomposition of adsorbed acetylene to formate ions after repeated heatings in H_2 .

This work should serve as a warning: unless new techniques are found to increase peak intensities and/or isolate individual species, tunneling spectroscopy shows little promise for the study of hydrocarbons on supported metal catalysts. Acetylene is one of the simplest hydrocarbons and the larger number of peaks in more complex species would make identification still more complicated and ambiguous.

EXPERIMENTAL METHODS

Here we present an outline of the experimental procedure; the interested reader is referred to references 24-26 for further details. The tunnel junctions were prepared on clean microscope slides by first evaporating 800 \AA thick aluminum strips in a vacuum of order 10^{-6} Torr. These were thermally oxidized in air to form the insulating barrier $25\text{-}30 \text{ \AA}$ thick. The substrates were returned to the vacuum chamber and cleaned in an argon glow discharge. The slides were then chilled to -125°C with liquid nitrogen and the palladium evaporated at pressures of $\sim 10^{-8}$ Torr. The amount evaporated, as measured by a quartz

crystal thickness monitor, was equivalent to a 4 \AA thick continuous layer. Fig. 1 shows an electron micrograph of the alumina surface uniformly covered by the palladium islands of average size 45 \AA .

While the slide was still cold, acetylene was introduced into the vacuum chamber at pressures of order 10^{-5} Torr and held at a constant pressure while the substrate was warmed to room temperature. The total acetylene exposure was approximately 2000 L ($1 \text{ L} = 1 \text{ Langmuir} = 10^{-6} \text{ Torr} \cdot \text{sec}$). After the acetylene was pumped out, the junctions were completed with the evaporation of a 2000 \AA thick lead cross strip as the top metal electrode.

The junctions were prepared in pairs, one with palladium particles, one without. A differential tunneling bridge was used to subtract the spectrum of the control junction from that of the doped one to minimize background features.²⁷ The tunneling spectrum of junctions without palladium did not show peaks due to adsorbed C_2H_2 (C_2D_2); thus, we found no evidence for acetylene bonded directly to clean alumina.

The completed junctions were mounted on a probe with electrical contacts and immersed into liquid helium. The tunneling spectrum, which is a plot of d^2V/dI^2 versus V , was taken using a modulation technique. For heating, the junctions were removed from liquid helium and warmed up to room temperature with pressurized dry air. They were then placed in an evacuated stainless steel "tee" and pressurized to 2.6×10^4 Torr (500 psi) with either hydrogen or deuterium. The "tee" was heated to $70 - 130^\circ \text{C}$ for times of order 5 - 15 minutes. After cooling, the junctions were returned to liquid helium for retracing.

We used Purified Grade acetylene (99.67%) obtained from Union Carbide with a dry ice-acetone trap on the gas line. The deuterated acetylene (Research Grade from U.S. Services, Inc.) was enriched to 99%. A mass spectrometer analysis of the gases showed negligible impurities.

RESULTS

The lower trace in Fig. 2 shows a tunneling spectrum for acetylene adsorbed on palladium particles supported by alumina. The top curve in this figure is a spectrum for the same junction after heating to 130° C in H₂. The spectra were obtained at saturation coverages of acetylene. The tunneling peak intensities are very low for these junctions; nevertheless, we have reproduced these experiments in 17 junctions. Attempts at increasing the palladium coverage to achieve higher signal intensities caused severe background problems.^{28,29}

Fig. 3 shows tunneling spectra for adsorbed deuterated acetylene before (lower trace) and after (upper two traces) repeated heatings in D₂. Generally, we found peaks in the deuterated spectra to be about a factor of two less intense than those we observed in the normal spectra (Fig. 2). Despite the low intensity, our results for the adsorption of deuterated acetylene on alumina supported palladium were reproducible in 12 junctions. This is clearly shown in Fig. 4 where tunneling spectra in the 25 - 200 meV range for deuterated acetylene obtained from three different junctions are displayed. These junctions were prepared under the same experimental conditions. Although the signal level is low, the peaks are clearly reproducible in both frequency and intensity.

Junctions that contain palladium particles but no acetylene (or deuterated acetylene) show no peaks due to the adsorption of background contaminants. Hence, the spectra presented here cannot be due to contamination in the junctions. This is confirmed by the isotope shifts observed in the spectra of junctions doped with acetylene.

DISCUSSION

A. Unheated $C_2H_2(C_2D_2)$

The observation of numerous CH(CD) and CC vibrational modes of varying frequencies in the lower trace of Fig. 2 (Fig. 3) clearly indicates the presence of many species on the surface. We attempted to isolate individual species by changing the $C_2H_2(C_2D_2)$ exposure as well as the palladium coverage, although these proved unsuccessful. The spectra presented here are at saturation acetylene coverages. Lowering the acetylene exposure or the palladium coverage resulted in overall lower signal intensities. As mentioned earlier, higher palladium coverages give rise to background problems.^{28,29}

The frequencies of the carbon-hydrogen (carbon-deuterium) stretching vibrations can be used to help characterize the state of hybridization of the adsorbed species. Acetylene, $C_2H_2(C_2D_2)$ is sp hybridized in the gas phase and has CH(CD) stretching vibrations between 407.8 and 418.4 (302.4 and 334.9) meV;³⁰ ethylene, $C_2H_4(C_2D_4)$ is sp^2 hybridized and has CH(CD) stretching vibrations between 370.6 and 385.1 (272.8 and 290.8) meV;³⁰ while ethane $C_2H_6(C_2D_6)$ is sp^3 hybridized and has CH(CD) stretching vibrations between 359.1 and 370.1 (258.3 and 277.1) meV.³⁰ Similarly, each of these species has a

characteristic CC stretching vibration: 244.8 (218.5) meV for acetylene, 201.2 (187.8) meV for ethylene and 123.4 (104.5) meV for ethane.³⁰ Peaks for CH bending (wagging, scissor, deformation, rocking, etc.) are in the 85 to 185 (75 to 145) meV region and are not well separated.³⁰ We have used these frequencies to guide us in the interpretation of the observed modes.

Before making the assignments of the observed modes, we need to discuss the effect of the top lead electrode. To date, despite many careful comparisons to optical data, no appreciable (> 1%) frequency shifts have been reported for adsorbed hydrocarbon molecules. Experiments by Kirtley and Hansma on the adsorption of benzoic acid on alumina showed that the frequency of all CC and CH vibrations were perturbed less than 0.5%.³¹ These results have now been confirmed for other hydrocarbon molecules.³² More recent investigations showed that low energy metal-carbon vibrations were sensitive to the top metal electrode, but CH vibrations were not appreciably affected.³³ Furthermore, numerous studies have found lead to be essentially inert and therefore the top electrode cannot be causing the observed chemistry.^{24-26,34}

Species A.

Of the many species present within the junction, weakly adsorbed acetylene is the easiest to identify. This is shown by peaks labeled A in the lower trace of Fig. 2 (79.1, ~ 90 (shoulder), 240.9, 409.3 and 431 meV). Gaseous acetylene has modes at 75.9 (symmetric CH bend) 90.5 (asymmetric CH bend),

244.8 (CC stretch), 407.8 (asymmetric CH stretch) and 418.4 (symmetric CH stretch).³⁰ Unfortunately, adsorbed deuterated acetylene is more difficult to detect (see Fig. 3, lower trace). Modes were observed at 58.7, 68, 211, 302 and 333 meV (gas phase modes at 62.6, 66.6, 218.5, 302.4 and 334.9 meV³⁰), although most of the intensity in this latter mode is clearly due to the OD stretch. The modes at 68, 211 and 302 meV are weak and were resolved in only 5 out of 12 spectra. The observed modes and their assignments are listed in Table 1.

It is unclear at this time how the acetylene is bonded in the junction environment; however, we can conclude that the molecule must interact with the palladium crystallites since we found no evidence for acetylene adsorption in clean alumina tunnel junctions. Unfortunately, we cannot use the intensity of these modes to help elucidate the structure or even the symmetry of the adsorbed species since there are essentially no selection rules in tunneling spectroscopy. There is a selection preference for modes that oscillate perpendicular to the plane of the tunneling barrier,²⁴⁻²⁶ but this is merely a preference, not a rigorous selection rule. Furthermore, experiments in a number of laboratories have shown that both infrared and Raman active modes are observed with comparable intensities.^{35,36}

The infrared spectrum of acetylene physisorbed on silica supported palladium has been reported ($\nu_{CH} = 403.0$ meV).¹³ Furthermore, acetylene weakly bonded to alumina has CC and CH(CD) stretching vibrations at 241.8 (215.7) and 399.3 (298.8) meV, respectively.^{37,38} This species is thought to be oriented

parallel to the surface. Migration of acetylene from the palladium crystallites to the alumina support is certainly possible in the tunnel junction environment.

Species B.

The peaks labeled B in the lower trace of Fig. 2 (96, 108.9, 178.5 and 381.0 meV) can be assigned to a rehybridized acetylenic species tightly bonded to the palladium clusters. Such metal-acetylene complexes are well known in organometallic chemistry³⁹ and a normal co-ordinate analysis has been performed for one such species $(C_2H_2Co_2(CO)_6)$.^{40,41} The assignments are listed in Table 1. Observation of a deuterated species with peaks at 77.3, 93.4, 158.9 and 287.6 meV in the lower trace of Fig. 3 is in agreement with these assignments.

Recent high resolution electron energy loss spectra of the low temperature adsorption of acetylene on a Pt(111) single crystal surface⁴² are in good agreement with the species observed here. These results are summarized in Table 1. Ultraviolet photoelectron spectroscopy has been used to characterize this adsorption system as well.^{20,21} The structure of the adsorbate has been interpreted as belonging to a rehybridized acetylenic species with a CC bond length of 1.26 \AA .²¹ A low-energy electron diffraction intensity analysis was insensitive to the CC bond length but placed the adsorbed acetylene 2.5 \AA above the outermost plane of platinum atoms and oriented parallel to the surface.⁴³ Diffraction data on model organometallic compounds containing acetylene yield carbon-carbon bond lengths intermediate between those for sp hybridized carbon atoms (CC triple bond,

1.20 Å) and sp^2 hybridized carbon atoms (CC double bond, 1.34 Å).³⁹ Similarly, the CCR (R = H, Ph, t - Bu, etc.) bond angle is intermediate between the 180° found for acetylene and the 120° in ethylene.³⁹

Species C.

From the peaks at 381.0 and 199.7 meV, labeled C in the lower trace of Fig. 2, and those at 287.6 and 186.9 meV in the lower trace of Fig. 3, we can conclude that an sp^2 hybridized species must also be present on the surface. The peaks at 144.0 and 160.6 (111.4 and 130.2) meV are most likely the CH (CD) bending vibrations associated with this species. An adsorbate of this type has been proposed as the predominant species formed from the chemisorption of acetylene on silica supported palladium.¹³ Our mode assignments are summarized in Table 1. The vibrational frequencies observed here correspond quite closely with those found in cis-1,2 dichloroethylene³⁰ (see Table 1). Kroeker, et al. have shown that halogen substituted hydrocarbons can be excellent model compounds for molecules adsorbed on metal surfaces.² From the characteristic frequencies observed in the vibrational spectra, one might expect CC bond lengths and CCH bond angles typical of those for sp^2 hybridized species: 1.34 Å and 120°, respectively. The exact bonding to the surface is still unknown.

Infrared spectroscopic studies of acetylene chemisorption on evaporated palladium films yields two distinguishable species intermediate between A and C ($\nu_{\text{CH}(\text{CD})} = 415.4$ (325.5) and 399.3 (311.2) meV, $\nu_{\text{CC}} = 233.1$ (214.5) and 229.4 (212.0) meV).^{17,18} A normal co-ordinate vibrational analysis of these species found the force constants to be insensitive to most structural parameters.¹⁸ Therefore, co-ordinated acetylene was assumed to be bent (C_{2v} symmetry) with CC and CH bond lengths of 1.28 and 1.074 Å, respectively. These values were chosen by analogy with the structure of several transition metal-acetylene complexes. The calculations were sensitive to CCH bond angle and the best fit value was found to be 140° .¹⁸

Species D.

The remainder of the peaks are rather difficult to assign; however, some general arguments can be made about other species possibly present in the junction environment. An sp^3 hybridized species (species D) may be found on the surface as indicated by peaks at 369.5 (287.6), 361.6 (263, shoulder); CH (CD) stretch and 122.3 (121.1): CC stretch. The mode at 169.9 (139.7) meV is most likely a CH(CD) bending mode associated with this species. The structural details of this species are only speculative at present.

sp^3 hybridized species have also been observed in the infrared spectra of acetylene chemisorbed on silica supported palladium particles. Studies by Clark and Sheppard show weak adsorptions at 368.2, 363.3 and 355.9 meV.¹⁶ More recent experiments by Dunken, et al. yield peaks at 367.7, 363.9 and

357.1 meV.³ Finally, Gates and Kesmodel¹⁹ observed a CH(CD) stretching vibration at 371.0 (278.9) meV for acetylene adsorbed on a Pd(111) single crystal surface using high resolution electron energy loss spectroscopy. All of these bands are characteristic of sp^3 hybridized species. These species may be either further rehybridized acetylene or adsorbed C_2H_n (where n is greater than 2) since self-hydrogenation is thought to be a facile process on palladium surfaces.⁴

Species E.

Finally, at least one other sp hybridized species (labeled E in the lower trace of Fig. 2) must be present on the surface. Since only hydrocarbons are present in the junction, the mode at 257.6 (234 meV) must belong to either a CH(CD) or CC vibration. This mode is 13 (15) meV higher in frequency than the CC stretching vibration of gaseous acetylene. These peaks may be evidence for a species of the form $H-C \equiv C-Pd/Al_2O_3$ where one end of the molecule is strongly interacting with the surface. Both the CC triple bond stretch and CH stretch in molecules of the form $HCCX$ ($X = CH_3, F, Cl, Br$)³⁰ or $(HCC)_n Y$ ($N = 3: Y = P, As, Sb; n = 4: Y = Si, Ge, Sn$)⁴⁴ are generally higher in frequency than those of gas phase acetylene. Furthermore, a small shoulder is observed on the high frequency side of the 409.3 meV peak, consistent with this interpretation.

Acetylene strongly adsorbed on alumina has been extensively studied by infrared spectroscopy.^{37,38} CC and CH(CD) stretching vibrations significantly up-shifted from gas phase acetylene were found at 248.9 (234.3) and 409.2 (318.7) meV, respectively.

These modes have been assigned to a $\text{H-C} \equiv \text{C-Al}_2\text{O}_3$ species oriented perpendicular to the surface. Again, C_2H_2 was not found to adsorb in a clean junction and therefore this species may either be bonded to the palladium islands or may be migrating from the metal crystallites to the alumina substrate.

Small shoulders or peaks in the 30 to 40 meV range observed in all of the spectra are probably due to the excitation of aluminum phonons.²⁵

B. Heated C_2H_2 (C_2D_2)

When the completed junctions containing acetylene (acetylene- d_2) were heated to 130 (110)° C in 500 psi of hydrogen (deuterium) for 10 - 15 minutes, the vibrational spectra changed dramatically. Hydrogen can diffuse through the top electrode to react with the hydrocarbons on the surface. Kroeker, et al. have previously observed hydrogenation of carbon monoxide on rhodium to form ethylidene in tunnel junctions that were heated in H_2 .²

The addition of hydrogen to acetylene chemisorbed on silica supported palladium crystallites results in the formation of surface alkyl groups ($\text{Pd}-(\text{CH}_2)_n-\text{CH}_3$, $n \geq 4$).¹³ These species were characterized by CH stretching vibrations at 360.8 and 353.4 meV. No such reaction products were observed here possibly due to the limited mobility of the adsorbates caused by the presence of the top lead electrode.⁴⁵

Analysis of the upper traces of Figs. 2 and 3 show the presence of formate ions in the junction (see Table 2). The breaking of the CC triple bond to form adsorbed formate ions

is consistent with the significant rehybridization of acetylene⁴⁶ as shown by the variety of species formed at room temperature in the junction environment. In spite of the heating in hydrogen, the surface species can react with the surface OH groups and be oxidized to formate ions when the CC triple bond breaks at elevated temperatures. These formate species may be bonded to the palladium crystallites or may be migrating from the metal to the alumina substrate. The close correspondence between the peaks observed from the adsorption of formic acid⁴⁷ on alumina and the peaks observed here is shown in Table 2. No mode assignments are listed since several of the assignments remain in question. We merely use the spectra of adsorbed formic acid and deuterated formic acid as a fingerprint. For more information on peak assignments, see reference 47.

The middle trace of Fig. 3 shows a spectrum of a completed junction heated to 80° C in 500 psi of D₂ for 5 minutes. The spectrum is only slightly different than the lower trace that is unheated and contains a mixture of deuterated sp, sp² and sp³ hybridized species. The growth of several peaks (most notably 208.0 and 285.6 meV) indicates the presence of at least one new surface species (possibly sp hybridized). The presence of a peak at 362.5 (CH stretch) is due to isotopic exchange with the support and may account for some of the new modes observed in this spectrum. Isotope exchange between adsorbed C₂D₂ and surface OH groups has been studied by infrared spectroscopy.^{37,38} The small peak shifts observed in the spectrum heated to 80° C are reproducible and may be caused by slight changes in the junction environment.

CONCLUSIONS

The tunneling spectroscopic study of acetylene chemisorption on alumina supported palladium particles lead to difficulties in the analysis of the results due to low peak intensities and to the formation of a variety of species. The low peak intensities may be due to the low coverage of the compound (about 50% of the surface is covered with palladium particles) and the tendency of electrons to tunnel between the particles. This would be difficult to overcome. The variety of species could, in principle at least, be decreased by in situ tunneling experiments where the spectra could be taken without warming the sample to room temperature before cooling it to cryogenic temperatures for measurement.⁴⁸

Although we could not isolate all of the species in the junction from the adsorption of acetylene on alumina supported palladium crystallites, we feel that we have a reasonable interpretation for most of the observed modes. Our assignments include weakly bonded acetylene, two types of strongly bonded acetylene and two other rehybridized species. Finally, peaks due to adsorbed formate ions were observed after heating the sample in hydrogen.

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Table 1: $C_2H_2(C_2D_2)$ Adsorbed on Palladium/Alumina: Unheated^a

Species A

Observed ^b		$C_2H_2(C_2D_2)^d$		$C_2H_2(C_2D_2)/Al_2O_3^e$		Assignment
79.1	(58.7)	75.9	(62.6)			CH(CD) bend
shoulder	(68)	90.5	(66.6)			CH(CD) bend
240.9	(211)	244.8	(218.5)	241.8	(215.7)	CC stretch
409.3	(302)	407.8	(302.4)	399.3	(298.8)	CH(CD) stretch
421	(333) ^c	418.4	(334.9)			CH(CD) stretch

Species B

Observed ^b		$C_2H_2Co_2(CO)_6(C_2D_2Co_2(CO)_6)^f$		$C_2H_2(C_2D_2)/Pt(111)^g$		Assignment
96.1	(77.3)	95.2	(74.6)	95	(71)	CH
108.9	(93.4)	110.8	(93.1)			CH(CD) bend
178.5	(158.9)	174.0	(166.9)	178	(156)	CC stretch
381.0	(287.6)	382.4 386.4	(264.8) (292.5)	375	(278)	CH(CD) stretch

Species C

Observed ^b		cis-CHClCHCl (CDClCDCl) ^d		Assignment
Shoulder	(68)	86.4	(67.0)	CH(CD) bend
144.0	(111.4)	146.2	(105.4)	CH(CD) bend
160.6	(130.2)	161.6	(130.3)	CH(CD) bend
199.7	(186.9)	196.8	(195.3)	CC stretch
381.0	(287.6)	380.9 381.5	(282.7) (288.3)	CH(CD) stretch

- a. All frequencies in meV. To convert to cm^{-1} , multiply by 8.065
- b. The peak positions are corrected for the superconducting energy gap of Pb (0.7 meV for 2 mV modulation)
- c. Most of this peak is due to OD stretch
- d. Reference 30
- e. References 37, 38
- f. References 40, 41
- g. Reference 42

Table 2: C₂H₂ and C₂D₂ Adsorbed on Palladium/Alumina: Heated^a

C ₂ H ₂ +H ₂ observed ^b	HCOO ⁻ /Al ₂ O ₃ ^c	C ₂ D ₂ + D ₂ observed ^b	DCOO ⁻ /Al ₂ O ₃ ^c
99.3	97.7	57	
106.3	116.6	77.3	86.8
130.8	130.6	95.6	96.7
142.3	143.3		112.2
157.3		118.7	116.6
171.8	170.2		128.1
188.3	182.1		169.0
200.3	197.8	186	182.8
341.8	339.6		198.4
356.3	358.3		253.4
369.3	372.7	263.0	265.8
		274.4	271.3
		286.9	

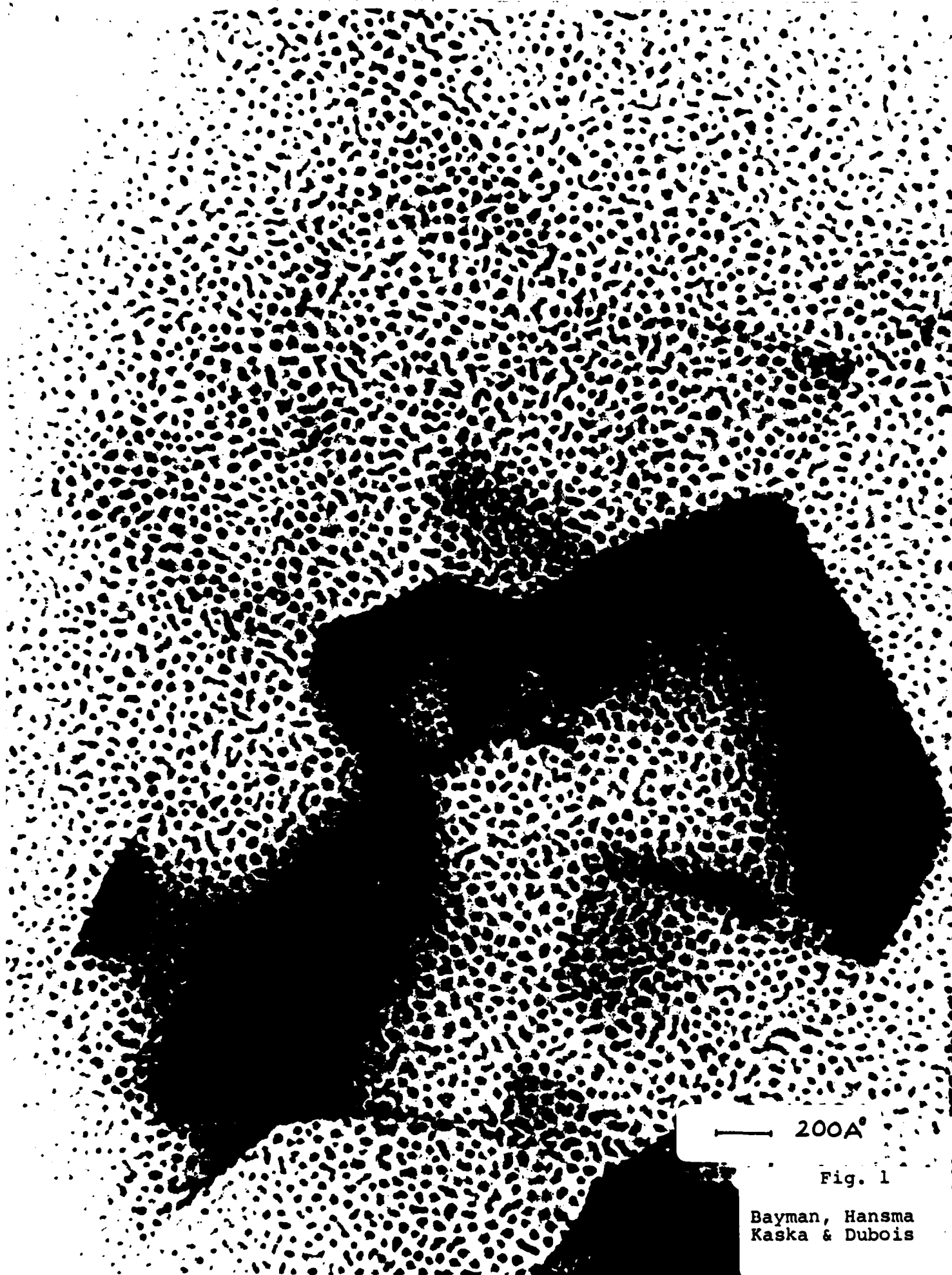
a. All frequencies in meV. To convert to cm⁻¹ multiply by 8.065

b. The peak positions are corrected for the superconducting energy gap of Pb (0.7 meV for 2 mV modulation)

c. Reference 47

FIGURE CAPTIONS

- Fig. 1 Transmission electron micrograph of palladium particles deposited on alumina. The particles are of 45 \AA average size and have uniform coverage over the alumina crystallites (which are the relatively large structures in the picture). This sample was prepared on a carbon-coated nickel grid with the same procedure as the junctions.
- Fig. 2 Differential tunneling spectra for C_2H_2 on palladium on alumina before (lower trace) and after (upper trace) heating in H_2 .
- Fig. 3 Differential tunneling spectra for C_2D_2 on palladium on alumina before (lower trace) and after (upper two traces) heating in D_2 .
- Fig. 4 The region from 25 ~ 200 meV of the differential tunneling spectra for C_2D_2 adsorbed on palladium on alumina obtained from three different junctions.



— 200A

Fig. 1

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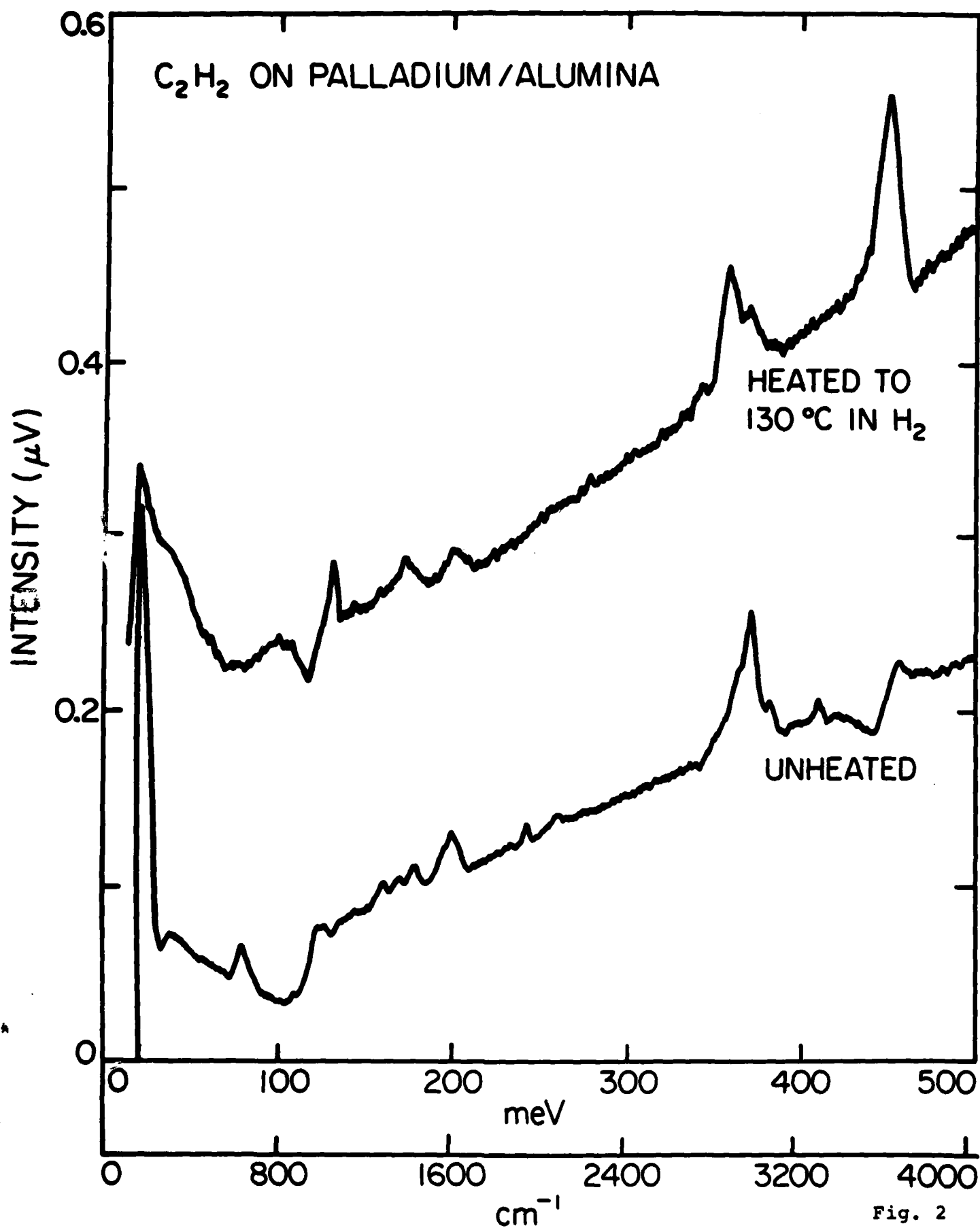


Fig. 2

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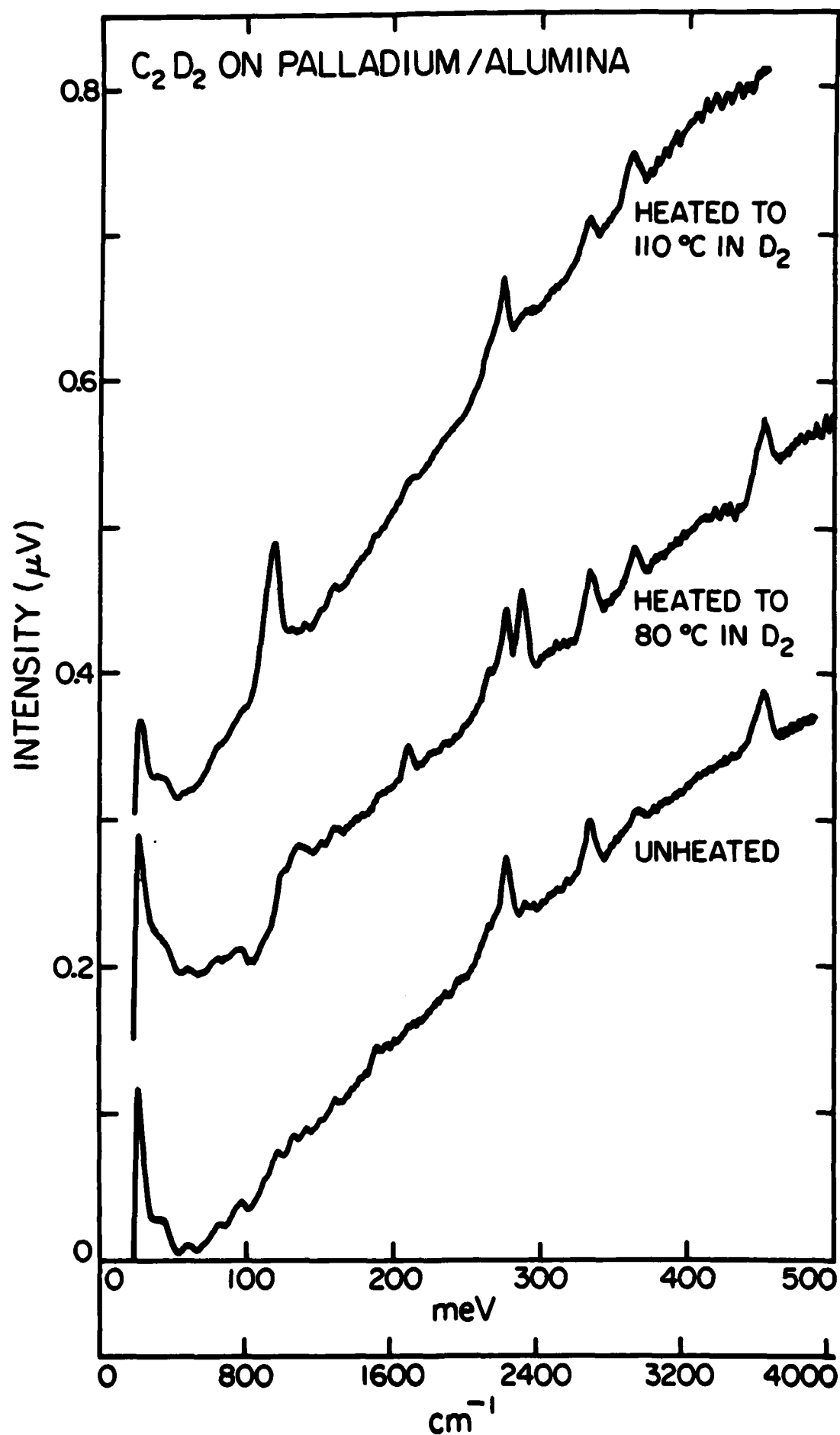


Fig. 3

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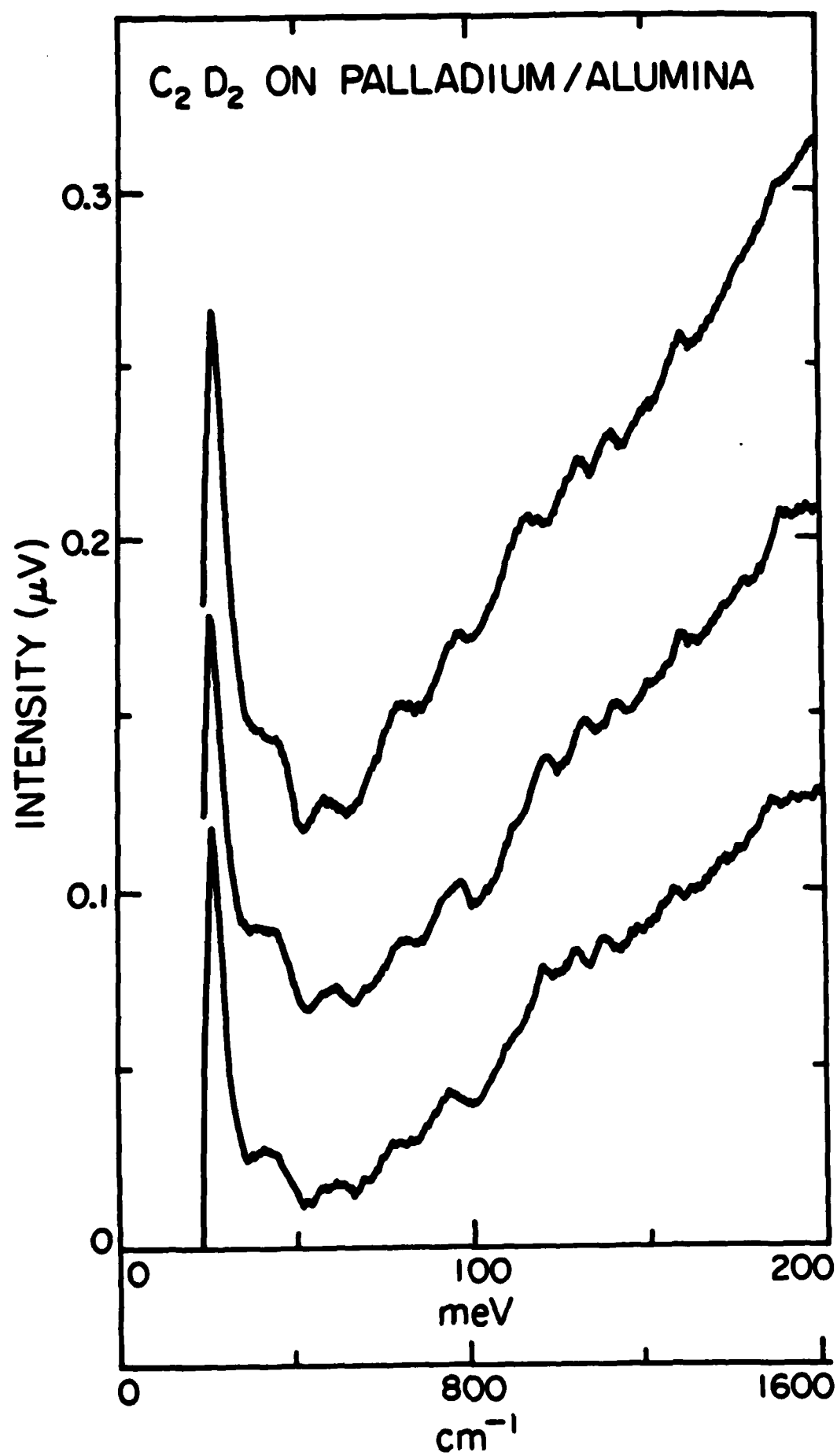


Fig. 4

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